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Utahin, a Ditropolonofuran

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Utahin is a yellow, optically inactive, high-melting compound (m.p. 313°, decomp.) which was isolated from the heartwood of *Juniperus utahensis* Lemm. by Runeberg[1] some years ago. It analysed for $C_{20}H_{20}O_5$ (M^+ 340) and forms a pale yellow diacetate, $C_{24}H_{24}O_7$.

From the spectral data and chemical properties discussed below it appears very likely that utahin is a symmetrical di-isopropylditropolonofuran (I), and thus the first ditropolonoid found in Nature. The formation of utahin probably involves the oxidative coupling of two simple tropolone molecules.

The i.r. spectrum of utahin (ref. 1, Figure 1) exhibits a broad, weak hydroxyl absorption between 3600 and 2300 cm.$^{-1}$ with a strong sharp band at 3250 cm.$^{-1}$ and a carbonyl band at 1620—1610 cm.$^{-1}$ similar to those of other tropolonoid compounds[2] possessing a characteristic intramolecular hydrogen bonding. A strong band around 1550 cm.$^{-1}$ corresponds to carbon–carbon double bond stretching vibration in tropolones.[2]

Utahin and its diacetate exhibit strong u.v. absorption below 440 and 400 nm., respectively (see ref. 1, Figure 2), with distinct patterns similar to those of tropolonoid systems[2] and particularly to that of the nitrous acid or sodium dichromate oxidation product (m.p. 303°, tentatively formulated as IIa) of 5-amino-4-isopropyltropolone (u.v. spectrum, see ref. 3, Figure Va).[4,5]

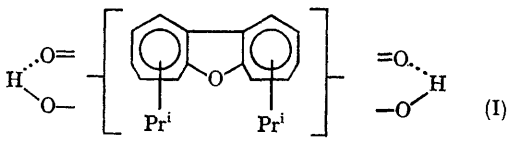
The mass spectrum of utahin[1] shows two distinct groups of fragments at m/e 340—253 and below m/e 128. The first group includes the following main fragments: M (340), $M - (2 \times 28)$, $M - (2 \times 28) - 15$, which may be assigned to the successive loss of two CO fragments followed by a methyl fragment. This indicates the presence of two tropolone nuclei in the utahin molecule. The mass spectra of simple isopropyltropolones [*e.g.*, β-thujaplicin (III)] exhibit similar characteristic fragments at $M - 28$ and $M - 28 - 15$.[6]

A distinct n.m.r. spectrum could not be obtained directly from utahin due to its low solubility. However, using a Varian C-1024 time averaging computer (CAT) a saturated deuteriochloroform solution of the compound gave a very clear and simple spectrum consisting of a doublet centred at 1·44 p.p.m.† (6 H; J 7 c./sec.) and a symmetrical multiplet at 3·79 p.p.m. (1 H; J 7 c./sec.) which could be assigned to the protons of an isopropyl group and two singlets at 7·52 p.p.m. (1 H) and 7·73 p.p.m. (1 H) attributable to protons attached to a tropolone ring. The signals of the ring protons of other tropolones occur at about the same field, for example β-thujaplicin (III) exhibits a signal group between 6·9 and 7·5 p.p.m. given by three protons The total integrated area of the signals in the utahin spectrum corresponds to only 9 protons. Therefore, utahin must be a symmetrical molecule containing 18 hydrogen atoms

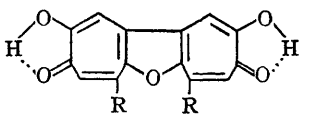
† Chemical shifts are given in p.p.m. from Me_4Si (internal standard).

attached to carbon and two hydroxylic protons whose signals were not observed in the recorded spectrum.

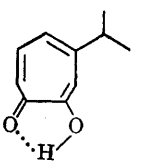
The signals at 7·52 and 7·73 p.p.m. due to the tropolone ring protons do not exhibit any significant coupling which suggests that the tropolone ring protons must be situated either β or γ to each other.



(I)



(II) a; R=Pr^i
b; R=Me



(III)

Utahin shows similar properties (high m.p., positive ferric chloride test, sparingly soluble orange sodium salt with aqueous sodium hydroxide) to those of the nitrous acid oxidation product of 5-hydroxy-4-methyltropolone tentatively formulated as (IIb) and of the aforementioned oxidation product (m.p. 303°) of 5-amino-4-isopropyltropolone assumed to possess structure (IIa).[4,5] A direct comparison (mixed m.p., i.r., and u.v.) of utahin with the latter compound (IIa) kindly carried out by Professor Shô Itô, Tôhoku University, leaves little doubt that the two compounds are identical.

The complete structure of utahin is now under investigation by means of *X*-ray crystallography.

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